

**CLAIMS**

1. A method of analysing a peptide by mass spectrometry, comprising the steps of: (a) reacting the peptide with a label to provide a derivatised peptide that, if the peptide contains an arginine residue, can form both a stabilised ion species ( $[P]^+$ ) and a protonated ion molecular species ( $[P+H]^+$ ) that differ by one average mass unit; and (b) analysing the derivatised peptide by mass spectrometry to provide a mass spectrum.
- 5 2. The method of claim 1, further comprising the step of: (c) analysing the mass spectrum to determine if it contains a peak pattern for a peptide in which a first monoisotopic mass peak and a second monoisotopic mass peak are separated by one average mass unit and in which the first peak is of lower mass than the second peak and is less abundant than the second peak.
- 10 3. A method of identifying a protein by mass spectrometry, comprising the steps of: (a) obtaining a mass spectrum of a mixture of peptides derived from a protein, wherein the peptides are derivatised with a label that provides derivatised peptides that, if the peptide contains an arginine residue, can form both a stabilised ion species ( $[P]^+$ ) and a protonated ion molecular species ( $[P+H]^+$ ) that differ by one average mass unit; (b) analysing the mass spectrum to identify if, after optional deisotoping , it contains a peak pattern for a peptide in which a first peak and a second peak are separated by one average mass unit and in which the first peak is less abundant than the second peak; and (c) searching a database using information generated in step (b) to identify the protein.
- 15 4. The method of claim 3, wherein step (b) includes identifying monoisotopic masses of the peptides, and step (c) uses the monoisotopic masses.
- 20 5. The method of any preceding claim, wherein the peptide is a proteolytic fragment.
6. The method of claim 5, wherein the peptide is a trypsin fragment.
7. The method of any preceding claim, wherein the derivatised peptide can form free radical ions.
- 25 8. The method of any preceding claim, wherein the label enhances the ionisation properties of the peptide relative to non-derivatised peptide.
9. The method of any preceding claim, wherein the label has formula (IIa), (IIb) (IVai), (IVaii), (IVaiii), (IVbii), (IVbiii), (IVaiv) and (IVbiv) described herein.
10. The method of any preceding claim, wherein the mass spectrometry uses a MALDI source.
- 30 11. The method of any preceding claim, wherein the mass spectrometry uses a TOF mass analyser.
12. The method of any preceding claim, wherein mass spectrometry output data is used to identify an amino acid sequence.
13. The method of claim 12, wherein the presence or absence of an arginine residue in a peak on a mass spectrum is used to reduce the number of possible identified amino acid sequences.
- 35 14. The method of any preceding claim, wherein the peptide is phosphorylated.

15. A peptide with an N-terminal residue and including an arginine residue, characterised in that (a) a label is attached to the N-terminal residue of the peptide and (b) the peptide can form both a stabilised ion species ( $[P]^+$ ) and a protonated ion molecular species ( $[P+H]^+$ ) that differ by one average mass unit.
- 5 16. The peptide of claim 15, comprising at least 5 amino acids.
17. The peptide of claim 15 or claim 16, in ionic and/or free radical form.
18. The peptide of any one of claims 15 to 17, wherein the peptide is phosphorylated.
19. A kit comprising: (a) a label for derivatisation of peptide(s) to provide derivatised peptides which, if the peptide contains an arginine residue, can form both a stabilised ion species ( $[P]^+$ ) and a protonated ion molecular species ( $[P+H]^+$ ) that differ by one average mass unit; and (b) one or more other components selected from the group consisting of: a separation medium, a protease, a protease inhibitor, a solvent, a buffer, a salt, a detergent, a mass standard and a matrix compound.
- 10 20. A system for analysing a mass spectrum, comprising a module for: (a) receiving a mass spectrum; and (b) analysing the mass spectrum to determine if, after optional deisotoping, it contains a peak pattern for a peptide in which a first peak and a second peak are separated by one average mass unit and in which the first peak is less abundant than the second peak.
- 15 21. The system of claim 20, which is a hardware system or a software system.
22. A computer program for analysing a mass spectrum, comprising a program module for: (a) receiving a mass spectrum; and (b) analysing the mass spectrum to determine if, after optional deisotoping, it contains a peak pattern for a peptide in which a first peak and a second peak are separated by one average mass unit and in which the first peak is less abundant than the second peak.
- 20 23. A method of analysing a deisotoped peptide mass spectrum, comprising the step of analysing the spectrum to determine if it contains a peak pattern for a peptide in which a first peak and a second peak are separated by one average mass unit and in which the first peak is less abundant than the second peak and has a lower mass than the second peak.
- 25 24. A method of screening for labels that can react with a peptide to provide a derivatised peptide that, if the peptide contains an arginine residue, can form both a stabilised cation ion species ( $[P]^+$ ) and a protonated ion molecular species ( $[P+H]^+$ ) that differ by one average mass unit, comprising the steps of: (a) obtaining a candidate label; (b) reacting the candidate label with an arginine-containing peptide to provide a derivatised arginine-containing peptide; (c) analysing the derivatised arginine-containing peptide by mass spectrometry to provide a mass spectrum; and (d) analysing the mass spectrum to determine if, after deisotoping, it contains a peak pattern for a peptide in which a first peak and a second peak are separated by one average mass unit and in which the first peak is less abundant than and has lower mass than the second peak.
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